arXiv:cond-mat/9809168v1 [cond-mat.str-el] 11 Sep 1998

typeset using JPSJ.sty <ver.1.0b>

A Model Study of the Low-Energy Charge Dynamics of NaV_2O_5

Satoshi NISHIMOTO[1] and Yukinori OHTA[1,2]

[1] *Graduate School of Science and Technology, Chiba University, Inage-ku, Chiba 263-8522*
[2] *Department of Physics, Chiba University, Inage-ku, Chiba 263-8522*

(Received September 11, 1998)

An exact-diagonalization technique on small clusters is used to calculate the dynamical density correlation functions of the dimerized t-J chain and coupled anisotropic t-J ladders (trellis lattice) at quarter filling, i.e., the systems regarded as a network of pairs (dimers or rungs) of sites coupled weakly via the hopping and exchange interactions. We thereby demonstrate that the intersite Coulomb repulsions between the pairs induce a low-energy collective mode in the charge excitations of the systems where the internal charge degrees of freedom of the pairs play an essential role. Implications to the electronic states of NaV_2O_5, i.e., fluctuations of the valence state of V ions and phase transition as a charge ordering, are discussed.

KEYWORDS: NaV_2O_5, charge dynamics, t-J model, intersite Coulomb, coupled ladders, trellis lattice

A compound α'-NaV_2O_5 discovered as an inorganic 'spin-Peierls' system[1)] has attracted much attention because of its intriguing charge degrees of freedom related to fluctuations of the valence state of V ions. It has been reported, e.g., that the ratio of the size of the spin gap at $T = 0$ K to the transition temperature is largely deviated from the BCS mean-field ratio as $2\Delta/k_{\rm B}T_c = 6.5$ with $\Delta = 9.8$ meV[2,3)] and $T_c = 34$ K,[1)] that a large amount of entropy is released at the phase transition in contrast to the case in $CuGeO_3$,[4,5)] and that anomalous behavior of the dielectric constant[6,7)] along the $\boldsymbol{a}$-axis occurs at T_c while no anomaly is observed along the $\boldsymbol{b}$-axis.[6)] Below T_c, a huge increase in the thermal conductivity has been reported to occur,[8)] and with a direct evidence, the charge-ordering scenario for the mechanism of the phase transition has been put forward from NMR experiment.[9)] Some possible ordering patterns of charges at $T < T_c$ have been suggested from theories.[10,11,12,13)] It has also been pointed out that the $\sim$1 eV features of the observed optical conductivity[15,14)] cannot be interpreted without assuming the system to be charge disproportionated even above T_c,[14,16)] and to be reconciled with the picture of the uniform valence of V ions which X-ray structural analyses have shown,[17,18,19)] we have argued that the rapid charge oscillation should exist in the system above T_c.[16)]

There are also a number of experiments detecting fluctuations above T_c. A recent line-shape analysis in the X-ray diffuse-scattering experiment[20)] suggests the pretransitional structural fluctuations to appear, where the correlation lengths start to increase around $\sim$50 K, $\sim$70 K, and above 90 K for the $\boldsymbol{c}$-, $\boldsymbol{a}$-, and $\boldsymbol{b}$-axes, respectively, and diverge as a power low by lowering temperature down to T_c. There has been an independent observation of the presence of critical scattering from soft phonons above T_c.[21)] Such a pretransitional effect has also been noticed in the ultrasonic experiment,[22)] where the anomalous behavior of sound velocity starts to develop at $\sim$80 K. Anomalous increase in the oscillator strength of the low-energy continuum observed at $T \simeq 150$ K in the optical conductivity experiment[14)] might also be related to this effect. All of these experimental data seem to suggest that to clarify the mechanism of the phase transition of this compound it should be of primary importance to study the nature of the fluctuations and ordering of electronic charges; we therefore consider this issue in the present paper.

The high-energy electronic states of the V-O network of the $(V_2O_3)^{3+}$ layer may be described by the d-p model with strongly-correlated d_{xy}-orbitals of V ions bridged by the p_x- and p_y-orbitals of O ions. Our analysis[12)] has shown that the low-energy states of the d-p model may be mapped to the t-J ladder model with strong anisotropy between legs and rungs. There exist interactions between ladders, and thus the generic model for the low-energy electronic states is the coupled anisotropic ladders described by the trellis-lattice t-J model at quarter filling.[12)] This system is a Mott insulator because of the strong anisotropy of the ladders:[12)] with increasing anisotropy the rung turns into an effective single site at half filling with a Hubbard repulsion.[23,24,12)] However, because the anisotropy is not extremely strong, the system cannot be regarded as the one-dimensional (1D) Mott insulator, as is evident in the significant deviations of the calculated single-particle spectral functions for the ladders with corresponding anisotropy from those for the single chain,[26,25)] although the spin degrees of freedom behave as a 1D Heisenberg chain with the effective antiferromagnetic exchange coupling.[27,17,12)] The rungs (or dimers) with their internal hopping and exchange interactions are thus the essential ingredient for the basic electronic states of the present system. A rung has two sites with one electron and is uniaxial in structure, and behaves as a 'repulsive-U center' with the effective Hubbard interaction $U_{\rm eff} = 2t - J$ (for a t-J dimer),[23)] which however has an internal charge degrees of freedom; i.e., the one-electron wave function is a linear combination of the two tight-binding basis functions located on the

left and right sites of the rung. The rungs are aligned in parallel on the two-dimensional (2D) plane to form the trellis lattice, and this configuration produces a unique interplay between charge and spin degrees of freedom, which we believe is the source of the observed anomalous behaviors of NaV_2O_5. Here the coupling between the rungs, especially the intersite Coulomb repulsions, plays an important role in the charge-ordering scenario for the mechanism of the phase transition.[11,12,13]

In this letter, we address the following question: suppose an assembly of such dimers and assume that the interaction between dimers is essentially the long-range Coulomb repulsion, then what is the charge dynamics of the assembly? We take two lattice models shown in Fig. 1: the 2D trellis lattice consisting of anisotropic ladders as a model for the $(V_2O_3)^{3+}$ layer of NaV_2O_5 and the 1D lattice with dimerization as a model for the rungs coupled in the direction perpendicular to the ladders of the trellis lattice. We will thereby show that the intersite Coulomb repulsions between the dimers induce a low-energy collective mode in the charge excitations of the systems which is due to the internal charge degrees of freedom of the dimers. We will then consider its relevance to the electronic states of NaV_2O_5 and present some consequences on the low-energy charge dynamics of this compound.

The Hamiltonian of our model systems is given by[12]

$$\begin{aligned} H = &- \sum_{\langle ij\rangle\sigma} t_{ij}\left(\hat{c}^{\dagger}_{i\sigma}\hat{c}_{j\sigma} + \text{H.c.}\right) \\ &+ \sum_{\langle ij\rangle} J_{ij}\left(\boldsymbol{S}_i\cdot\boldsymbol{S}_j - \frac{1}{4}n_i n_j\right) \\ &+ \sum_{<ij>} V_{ij} n_i n_j, \end{aligned} \tag{0.1}$$

where $\hat{c}^{\dagger}_{i\sigma} = c^{\dagger}_{i\sigma}(1-n_{i,-\sigma})$ is the constrained electron-creation operator at site i and spin σ $(=\uparrow,\downarrow)$, $n_i = n_{i\uparrow}+n_{i\downarrow}$ is the electron-number operator, $\boldsymbol{S}_i$ is the spin-$\frac{1}{2}$ operator, and $\langle ij\rangle$ represents a pair of neighboring sites i and j. We restrict ourselves to the case of quarter filling. We define the hopping and exchange parameters t_{ij} and J_{ij} as $t_\perp$ and $J_\perp$ for the rungs and $t_\parallel$ and $J_\parallel$ for the legs, respectively, and also as t_{xy} and J_{xy} for the zigzag-chain bonds where the intersite Coulomb repulsions V_{xy} is also taken into account. For the 1D chain model, we define the parameters for alternating bonds as $t_\perp$ and $J_\perp$ for stronger bonds and t_{xy} and J_{xy} for weaker bonds. We include V_{xy} only in the latter bonds. We use values of the ladder parameters obtained in ref.:[12] $t_\perp = 0.298$, $t_\parallel = 0.140$, $J_\perp = 0.0487$, and $J_\parallel = 0.0293$ in units of eV. The value $t_{xy} = 0.05$ eV is assumed and the relation $J_{xy} = 4t^2_{xy}/U_d$ is used for simplicity to obtain the value of J_{xy}. The value of V_{xy} is then varied for simulating various situations. The repulsion $V_\parallel$ on the leg bonds is also taken into account for some discussions. We employ a Lanczos exact-diagonalization technique on small clusters to calculate the ground state and excitation spectra of the systems. We take a cluster of coupled four 2×2 ladders (or 2×2 unit cells) with periodic boundary condition for the trellis-lattice model and a 16-site (or 8 unit cell) ring for the 1D dimerized lattice model.

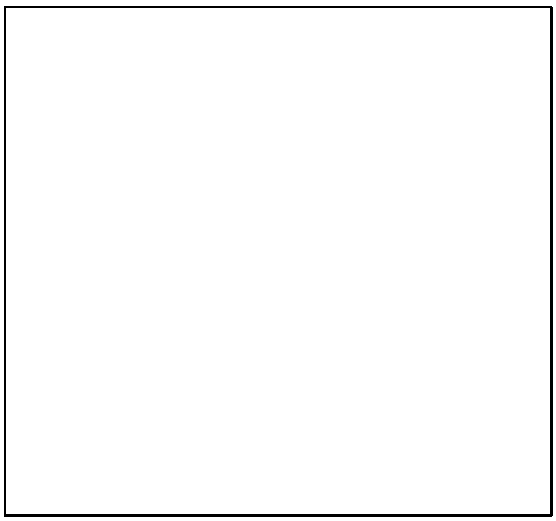

Fig. 1. Schematic representation of the lattice structures of (a) the trellis lattice t-J model and (b) the 1D dimerized t-J model. The rungs in (a) and dimers in (b), which have the strongest hopping and exchange interactions, are indicated by bold lines.

A direct way for examining the charge dynamics of the systems may be to calculate the dynamical density correlation function defined by

$$C(\boldsymbol{q},\omega) = \sum_{\nu>0} |\langle\psi_\nu|\rho_{\boldsymbol{q}}|\psi_0\rangle|^2\,\delta(\omega-(E_\nu-E_0)), \tag{0.2}$$

where $\rho_{\boldsymbol{q}}$ is the Fourier transform of the electron-number operator, and E_ν and $|\psi_\nu\rangle$ are respectively the ν-th eigenenergy and eigenstate of the system (with the ground state denoted by $\nu = 0$). We have examined the individual excitations of electrons by the optical conductivity calculations,[16] whereas by the present $C(\boldsymbol{q},\omega)$ calculations one can find possible low-energy collective excitations as well.

Now let us first examine the calculated results for the 1D dimerized t-J model. The results are shown in Fig. 2, where the parameter values used are in the region of strong dimerization $t_\perp/t_{xy} = 5.96$ and thus the charge gap clearly opens.[23] We immediately find here that at $V_{xy} = 0$ the spectra are the ones consistent with particle-hole transitions across the charge gap but with increasing the value of V_{xy} there appears the low-energy peak at $q = 0$ which is smoothly connected to the higher-energy peaks at larger momenta with a well-defined dispersion $\omega_{\boldsymbol{q}}$, the width of which scales with V_{xy}. We thus find a collective-mode–like behavior in the spectra. Although not related to the present issue, we find for very large values of V_{xy} ($\gtrsim 1$ eV) that there appears a set of low-energy peaks at $\omega \lesssim 0.2$ eV, the position and weight of which are almost momentum-independent; this feature becomes dominant for $V_{xy} \gtrsim 2$ eV and is simply a consequence of the stabilization of the state with two electrons in a dimer, as is naturally expected by intuition.

Similar spectral features are also found in the trellis lattice model (see Fig. 3) although the results are only for

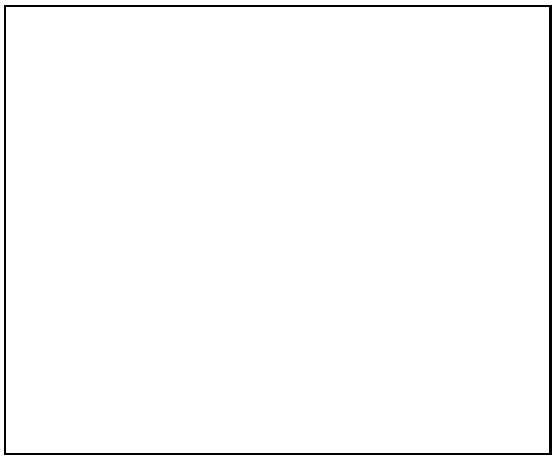

Fig. 2. Dynamical density correlation function $C(q,\omega)$ calculated for the 1D dimerized t-J model with the parameter values of $t_\perp$, t_{xy}, $J_\perp$, and J_{xy} listed in the text. All the δ-functions in Eq. (2) are Lorentzian broadened with the width of 0.03 eV.

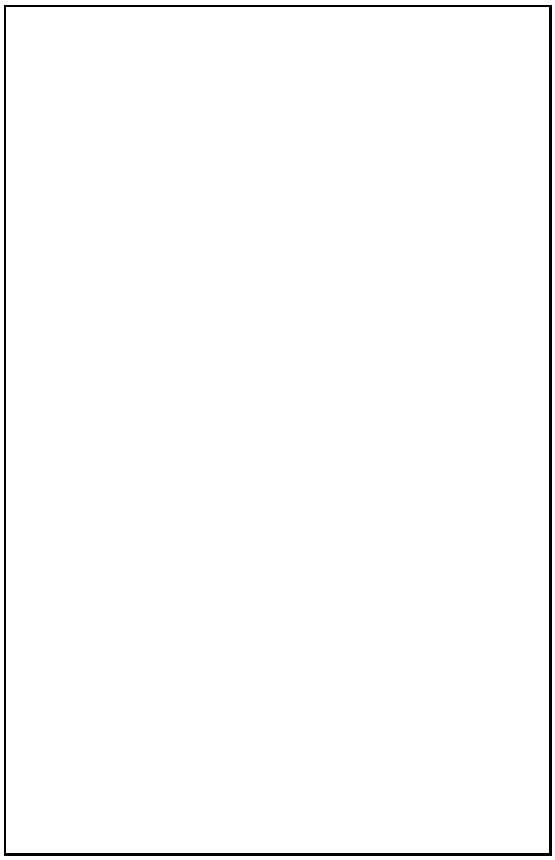

Fig. 3. Dynamical density correlation function $C(\boldsymbol{q},\omega)$ calculated for the trellis-lattice t-J model. The momentum $\boldsymbol{q} = (q_\perp, q_\parallel)$ is shown in each panel.

the momenta $\boldsymbol{q} = (0,0)$, $(\pi,0)$, $(0,\pi)$, and (π,π) where the spectra for the latter two momenta are equivalent due to symmetry. We find that the features reflecting individual excitations at small V_{xy} values gradually change into the features resembling a collective-mode excitation by increasing V_{xy} values, i.e., the low-energy peak at $\boldsymbol{q} = (0,0)$ which 'connects' with the higher-energy peak at $\boldsymbol{q} = (\pi,0)$ and $(0,\pi)$, where the width of the dispersion $\omega_{\boldsymbol{q}}$ again scales with V_{xy}. If we also include the repulsion $V_\parallel$ in the legs of the ladders, we find that the lowest-energy peak shifts to the nonzero momenta $\boldsymbol{q} = (0,\pi)$ and (π,π) as shown in Fig. 4, the behavior being naturally expected from simple consideration of the repulsion between two electrons. Thus, either 'ferroelectric' or 'antiferroelectric' fluctuation with corresponding dispersion $\omega_{\boldsymbol{q}}$ is realized depending on the relative strength of the intersite repulsions; other types of fluctuations would also be realized if we include some longer-range repulsions. These observations are quite natural because the parameters we are working with are in the region where the long-range charge order appears in the infinite systems, as the calculated values of the equal-time charge correlations $\langle n_i n_j \rangle$ directly indicate (where there should be a critical repulsive strength V_c),[12] and thus we should observe the features corresponding to the Goldstone mode at $V > V_c$, although in finite-size systems no real symmetry-breaking occurs and thus there is no exactly zero-energy excitation.

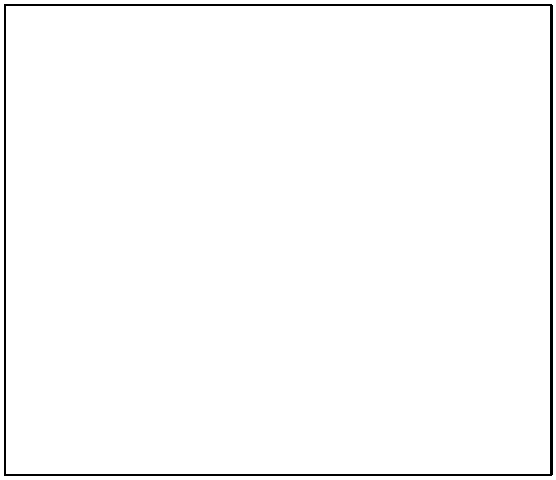

Fig. 4. As in Fig. 3 but for the case with nonzero values of the repulsion $V_\parallel$.

A speculation to what happens at $T > 0$ in the thermodynamic limit seems to be straightforward from the results given above. With increasing temperature from 0 K the thermal fluctuations in the long-range charge-ordered state develop and at $T = T_c$ there occurs a phase transition. The fluctuations of charges would be remnants of the quantum fluctuations obtained for small clusters at $T = 0$ K where the charges oscillate coherently between left and right sites of the rungs using their internal degrees of freedom. The phase transition would be of a classical order-disorder type as in the theory of

ref.[10] where the result of a 2D Ising model was used, and would thus be of the second order. Here we should note that the effective local-field and thus local order parameter for the charge ordering persists even well above T_c as we have demonstrated via the optical conductivity calculations[14,16] where we used the term 'charge disproportionation'. In other words, we have the local order parameter as the spatial left/right shift of the electron in the rung (which is nonvanishing even at high temperatures) and its thermal (and quantum) fluctuations characterize the electronic state of the system. This is thus quite unlike, e.g., the usual charge-density-wave transition where the normal fermi-liquid is recovered immediately above T_c and the location of the fermi momentum $\boldsymbol{k}_{\rm F}$ plays an essential role. In the present system, the large charge gap exists, and there is no metallic screening of long-range Coulomb interactions. At temperatures far above T_c, say at room temperature, the local order parameters would be in a state of rapid and random oscillations without coherence, but with lowering temperature, the spatial correlation develops, and the correlation length increases and diverges as the temperature approaches T_c where the long range order comes out. From experimental data which we have summarized above,[20,21,22,14] one may expect that the temperature at which the coherent fluctuations start to develop would be in a range of $T \simeq 50 - 150$ K. The character of the fluctuations, i.e., ferroelectric, antiferroelectric, or whatever, would have a consequence on the charge-ordering pattern at $T < T_c$, and needs to be clarified further from both experiment and theory. We should note that the lattice degrees of freedom may well play a role in the fluctuations of charges. A recent study of the local Holstein and/or Peierls couplings in the 1D chain and ladder models[28] seems quite suggestive, although nonadiabatic treatment will be essential for treating the slow order-parameter fluctuations with a time scale compatible with the lattice fluctuations. As for the spin degrees of freedom, it is on one hand an open question whether the uniform susceptibility in such a charge state fits well to the Bonner-Fisher curve[29] with significant deviations below 250 K,[30] but on the other hand the charge-ordering pattern would naturally explain the origin of the spin gap at $T < T_c$.[11,12,13] Actual determination of the pattern would however be an intricate problem because not only the long-range nature of the Coulomb interaction but also the lattice degrees of freedom seem to play an important role.[13] Suggestions from experiment are most desirable.[31] Finally, let us remark on the submillimeter-wave ESR experiment by which a direct observation of the spin gap has recently been made successfully.[32] We here would like to suggest that if the mechanism of the spin-gap opening is due to local spin-singlet formation by the charge ordering[9,11,13] and if the slow fluctuations leading to the charge-ordering instability present well above T_c, the fast time-scale measurement like this ESR experiment could possibly detect the 'spin gap' even above T_c which is continuous to the spin gap below T_c. So far, neutron scattering experiments have not found such signals.[2,3]

In summary, we have calculated the dynamical density correlation function of the 1D dimerized t-J model and trellis lattice t-J model at quarter filling using an exact-diagonalization technique on small clusters, whereby we demonstrate that the intersite Coulomb repulsions between the dimers (or rungs) induce a low-energy collective mode in the charge excitations of the systems where the internal charge degrees of freedom of the dimers (or rungs) play an essential role. We have argued that the electronic states and charge ordering of NaV_2O_5 should be understood in terms of the fluctuations of the local order parameters representing the electron locations in the rungs, and have discussed the experimental consequences of the fluctuations.

We would like to thank A. N. Vasil'ev and T. Ohama for enlightening discussions on the experimental aspects of NaV_2O_5. Financial support for S. N. by Sasakawa Scientific Research Grant from the Japan Science Society and for Y. O. by Iketani Science and Technology Foundation are gratefully acknowledged. Computations were carried out at Computer Centers of the Institute for Solid State Physics, University of Tokyo and the Institute for Molecular Science, Okazaki National Research Organization.

[1] M. Isobe and Y. Ueda: J. Phys. Soc. Jpn. **65** (1996) 1178.
[2] Y. Fujii *et al.*: J. Phys. Soc. Jpn. **66** (1997) 326.
[3] T. Yosihama *et al.*: J. Phys. Soc. Jpn. **67** (1998) 744; T. Yosihama *et al.*: Physica B **234-236** (1997) 539.
[4] M. Köppen *et al.*: Phys. Rev. B **57** (1998) 8466.
[5] D. K. Powell *et al.*: Phys. Rev. B **58** (1998) R2937.
[6] Y. Sekine, N. Takeshita, N. Môri, M. Isobe, and Y. Ueda: preprint.
[7] A. I. Smirnov *et al.*: cond-mat/9808165.
[8] A. N. Vasil'ev *et al.*: Phys. Rev. Lett. **81** (1998) 1949.
[9] T. Ohama, H. Yasuoka, M. Isobe, and Y. Ueda: preprint (1998).
[10] P. Thalmeier and P. Fulde: cond-mat/9805230.
[11] H. Seo and H. Fukuyama: J. Phys. Soc. Jpn. **67** (1998) 2602.
[12] S. Nishimoto and Y. Ohta: J. Phys. Soc. Jpn. **67** (1998) in press.
[13] M. V. Mostovoy and D. I. Khomskii: cond-mat/9806215.
[14] A. Damascelli *et al.*: Phys. Rev. Lett. **81** (1998) 918; A. Damascelli *et al.*: cond-mat/9806222.
[15] S. A. Golubchik *et al.*: J. Phys. Soc. Jpn. **66** (1997) 4042.
[16] S. Nishimoto and Y. Ohta: cond-mat/9808061.
[17] H. Smolinski *et al.*: Phys. Rev. Lett. **80** (1998) 5164.
[18] H. G. von Schnering *et al*: Z. Kristallogr. **213** (1998) 246.
[19] A. Meetsma, J. L. de Boer, A. Damascelli, T. T. M. Palstra, J. Jegoudez, and A. Revcolevschi: Acta Cryst. in press.
[20] S. Ravy *et al.*: cond-mat/9808313.
[21] H. Nakao *et al.*: Physica B **241-243** (1998) 534.
[22] P. Fertey *et al.*: Phys. Rev. B **57** (1998) 13698.
[23] S. Nishimoto and Y. Ohta: cond-mat/9805280.
[24] S. Nishimoto and Y. Ohta: J. Phys. Soc. Jpn. **67** (1998) 2598.
[25] S. Nishimoto and Y. Ohta: unpublished.
[26] J. Riera, D. Poilblanc, and E. Dagotto: cond-mat/9804209.
[27] P. Horsch and F. Mack: Euro. Phys. J. B **5** (1998) in press (No. 5).
[28] J. Riera and D. Poilblanc: cond-mat/9809028.
[29] J. G. Bonner and M. E. Fisher: Phys. Rev. **135A** (1964) 640.
[30] J. Hemberger *et al.*: Europhys. Lett. **42** (1998) 661.
[31] T. Chatterji, K. D. Liß, G. J. McIntyre, M. Weiden, R. Hauptmann, and G. Geibel: Solid State Commun. in press.
[32] S. Luther, H. Nojiri, M. Motokawa, M. Isobe, and Y. Ueda: preprint.

This figure "fig1.gif" is available in "gif" format from:

http://arXiv.org/ps/cond-mat/9809168v1

This figure "fig2.gif" is available in "gif" format from:

http://arXiv.org/ps/cond-mat/9809168v1

This figure "fig3.gif" is available in "gif" format from:

http://arXiv.org/ps/cond-mat/9809168v1

This figure "fig4.gif" is available in "gif" format from:

http://arXiv.org/ps/cond-mat/9809168v1